Supporting Information

Polyoxometalates-doped TiO_2/Ag hybrid heterojunction: removal of multiple pollutants and mechanism investigation

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Characterization

The morphology and detailed structure of the samples were observed with a JEOL JSM 4800F SEM with an energy-dispersive X-ray (EDX) spectrometer and TEM operating at 200 kV. The intermediates for degradation of 2,4-DCP were detected by mass spectrometry (thermoscientific). XPS plots were obtained using an Al monochromatic source (ESCALABMKII spectrometer, 1.486 keV). Absorption spectrum was obtained with a UV-Vis spectrometer (Shimadzu UV-2600). Surface areas (BET) were analyzed using a Micromeritics Autosorb IQ instrument. X-Ray diffraction (XRD) patterns were examined with filtered Cu Kα radiation (Bruker AXS D8 Focus, λ= 1.54056 Å). A Hitachi F-4600 spectrophotometer was used to obtain the photoluminescence (PL) spectra of the catalyst. The electron paramagnetic resonance (EPR) was measured with a JEOL JES-FA200 spectrometer.

Chemicals

All chemicals were used without any further purification. $NaVO_3$ (99.0 %), Na_2HPO_4 (99.0 %) and poly (ethylene glycol)-block-poly (propyl-ene glycol)-block-poly (ethylene glycol) (P123) were purchased from Aladdin Chemical Co., Ltd. $Na_2MoO_4 \cdot 2H_2O$ (99.0 %), isopropyl titanate (99.9 %), $BaSO_4$ (99.0 %), isopropanol (AR) and triethanolamine (99.5 %) were provided by Macleans. $AgNO_3$ (99.8 %), Na_2SO_4 (99.0 %), tetracycline, 4-hydroxy-TEMPO (99.0 %) and methyl orange (AR) were purchased from China Sinopharm Chemical Reagent Co., Ltd. $K_2Cr_2O_7$, 2,4-difluorophenol. 2,4-dichlorophenol, 2,4-dibromophenol and hexafluorobisphenol A were obtained from Bailingwei Technology Co., Ltd.

Preparation of $H_5PMo_{10}V_2O_{40}$

24.4 g sodium metavanadate was dissolved in 100 ml boiling water. 7.1 g Na_2HPO_4 was dissolved in 100 ml of water and added to the above solution. After the solution is cooled, 5 ml of concentrated sulfuric acid was introduced, and the solution turns red. 121 g of $NaMO_4 \cdot 2H_2O$ was dissolved in 200 ml of aqueous solution and added to the mixed solution. Add 85 ml of concentrated H_2SO_4 into the mixture under intense agitation. When the mixed solution is cooled to room temperature, 500 ml of ether was used to extraction. The red solid powder of POM is obtained by collecting the ether layer and passing air into it to drive away the ether.

Preparation of $Ti_{2.5}PMo_{10}V_2O_{40}$-$TiO_2$ composites

1.25 g of P123 and a certain amount of $H_5PMo_{10}V_2O_{40}$ (10 - 20 mol % relative to isopropyl titanate) were dissolved in 40 ml aqueous solution ($V_{water} : V_{ethanol} = 3:1$, pH = 1.5). Then 3 g of isopropyl titanate was added drop-wise to the above solution under vigorous magnetic stirring in which the pH of the solution is maintained at approximately 1.5 using sulfuric acid or ammonia. The reaction was continued for 2 h to obtain a colloidal precipitate that was then aged at 70 °C for 5 hours. The resulting precipitate was dried at 90 °C after centrifuging and washing and then calcined at 400 °C for 1 h in a muffle furnace to obtain a precursor (*abbr.* PMoV-TiO_2).

Active species trapping experiment

Triethanolamine (TEOA), 4-hydroxy-TEMPO and isopropanol (IPA), as hole (h^+), superoxide radical ($\cdot O_2^-$) and hydroxyl radical ($\cdot OH$) scavengers respectively, were added to the 2,4-DCP degradation system. The following processes were similar to the 2,4-DCP photodegradation experiment.

Photoelectrochemical and Electrochemical measurements

Photocurrent performance was tested with a 300 W Xe lamp and a CHI660E Electrochemical Workstation in a conventional three electrode cell, using Hg/Hg_2Cl_2 and a Pt wire electrode were served as reference electrode and the counter electrode, respectively. The working electrode was prepared on 1×4 cm^2 FTO glass that has an active area of *ca.* 3 cm^2. Next, 50 mg of the as-prepared samples and 0.2 ml naphthol were dispersed into 3 mL of ethanol. Then take 3ml suspension and drop it evenly onto the working electrode. The EIS measurements was characterized with a frequency range from 0.01 Hz to 10 kHz at -0.3 V in 0.2 M Na_2SO_4 solution.

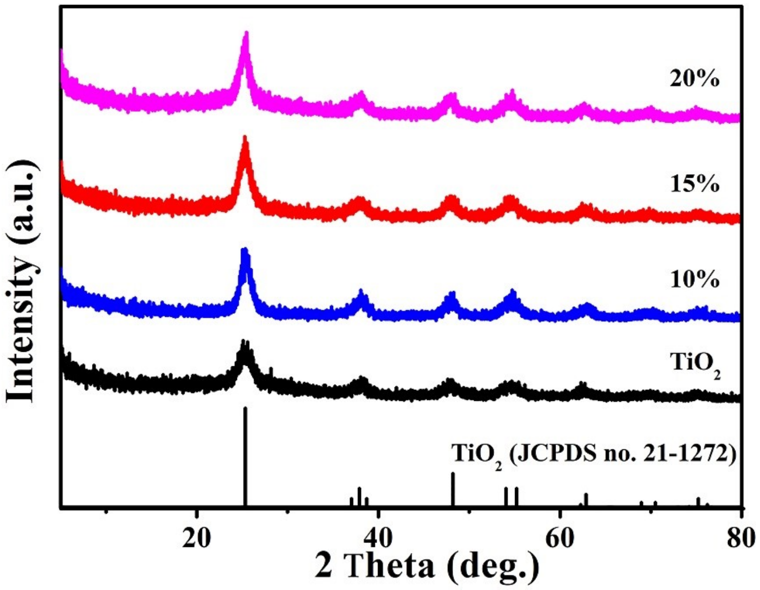


Figure S1. The PXRD patterns of different molar ratio of $H_5PMo_{10}V_2O_{40}$ to isopropyl titanate.

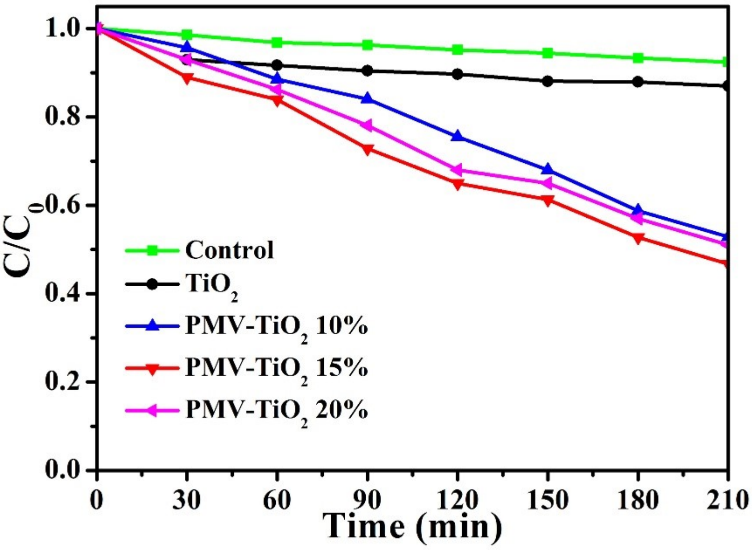
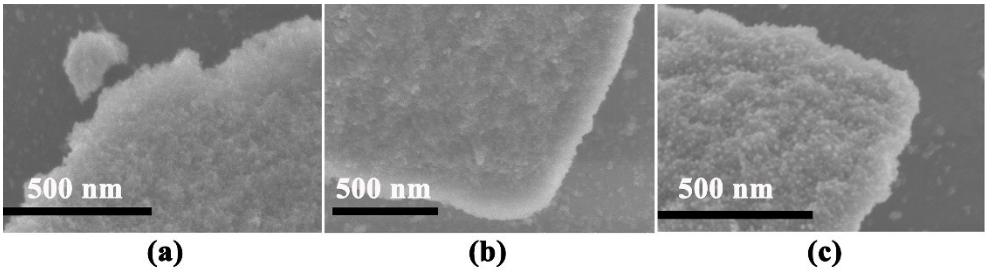
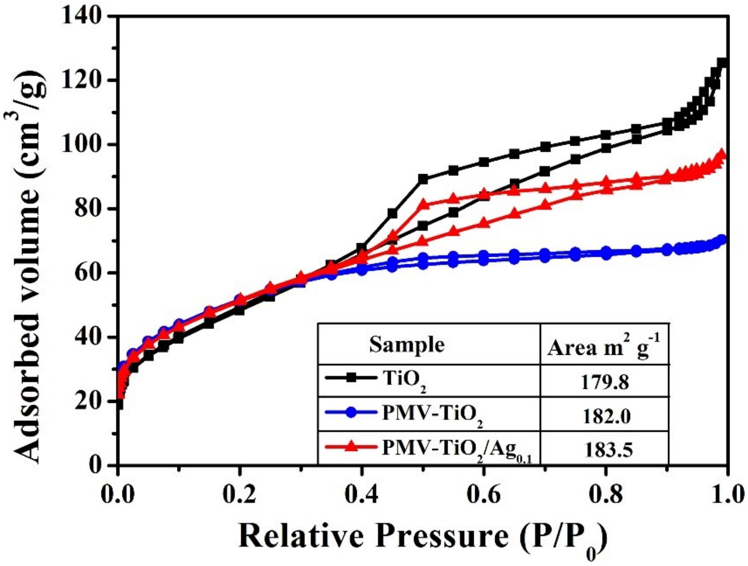


Figure S2. The profiles of photodegradation of 2,4-dichlorophenol by different molar ratio of PMV-TiO_2 under visible-light (λ >420 nm).



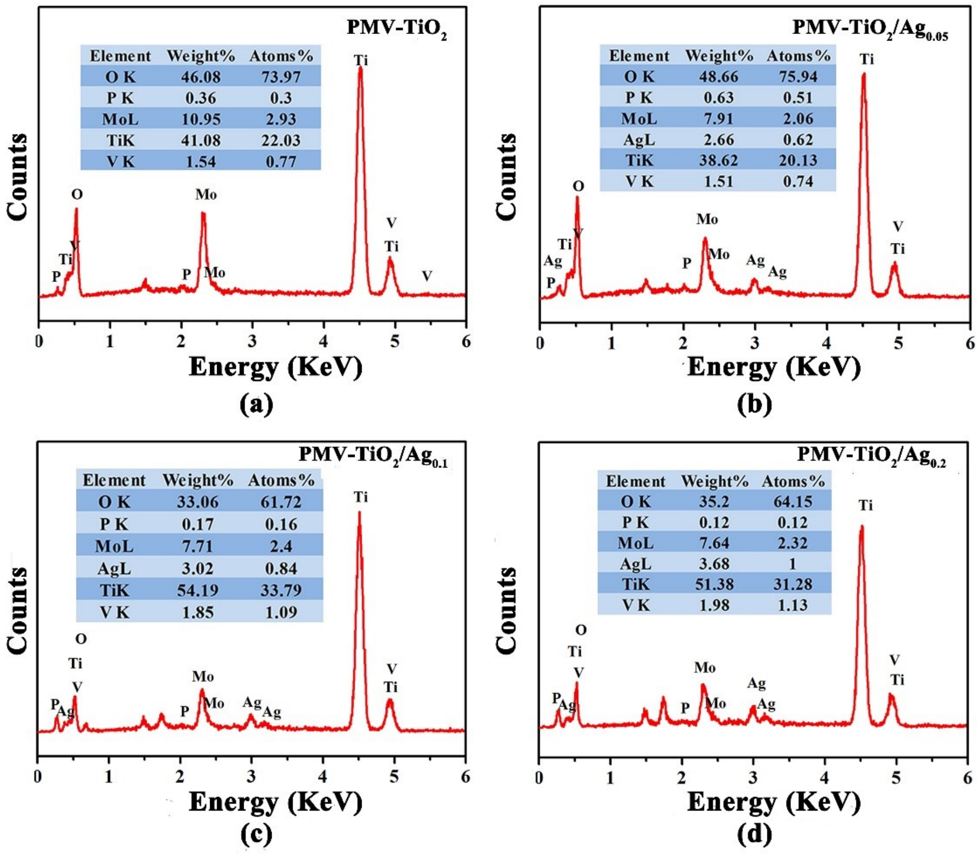
(a) (b) (c)

Figure S3. The SEM images of (a) TiO_2 and (b) PMV-TiO_2 and (c) PMV-TiO_2/$Ag_{0.1}$.



Sample	Area m^2 g^{-1}
TiO_2	179.8
PMV-TiO_2	182.0
PMV-TiO_2/$Ag_{0.1}$	183.5

Figure S4. The N_2 adsorption-desorption isotherms of TiO_2, PMV-TiO_2 and PMV-TiO_2/$Ag_{0.1}$.



PMV-TiO_2

Element	Weight%	Atoms%
O K	46.08	73.97
P K	0.36	0.3
MoL	10.95	2.93
TiK	41.08	22.03
V K	1.54	0.77

PMV-TiO_2/$Ag_{0.05}$

Element	Weight%	Atoms%
O K	48.66	75.94
P K	0.63	0.51
MoL	7.91	2.06
AgL	2.66	0.62
TiK	38.62	20.13
V K	1.51	0.74

PMV-TiO_2/$Ag_{0.1}$

Element	Weight%	Atoms%
O K	33.06	61.72
P K	0.17	0.16
MoL	7.71	2.4
AgL	3.02	0.84
TiK	54.19	33.79
V K	1.85	1.09

PMV-TiO_2/$Ag_{0.2}$

Element	Weight%	Atoms%
O K	35.2	64.15
P K	0.12	0.12
MoL	7.64	2.32
AgL	3.68	1
TiK	51.38	31.28
V K	1.98	1.13

Figure S5. EDX of (a) PMV-TiO_2; (b) PMV-TiO_2/$Ag_{0.05}$; (c) PMV-TiO_2/$Ag_{0.1}$; (d) PMV-TiO_2/$Ag_{0.2}$, respectively.

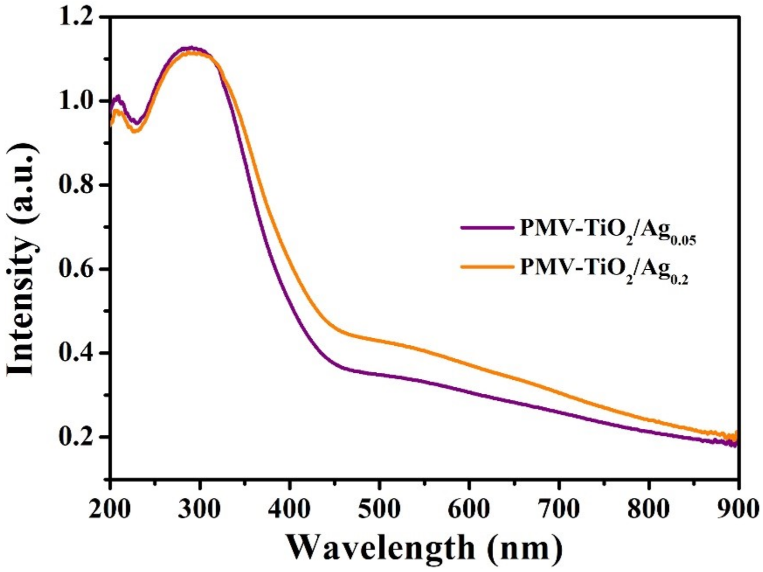


Figure S6. The DRS for PMV-TiO$_2$/Ag$_x$ (x = 0.05, 0.2).

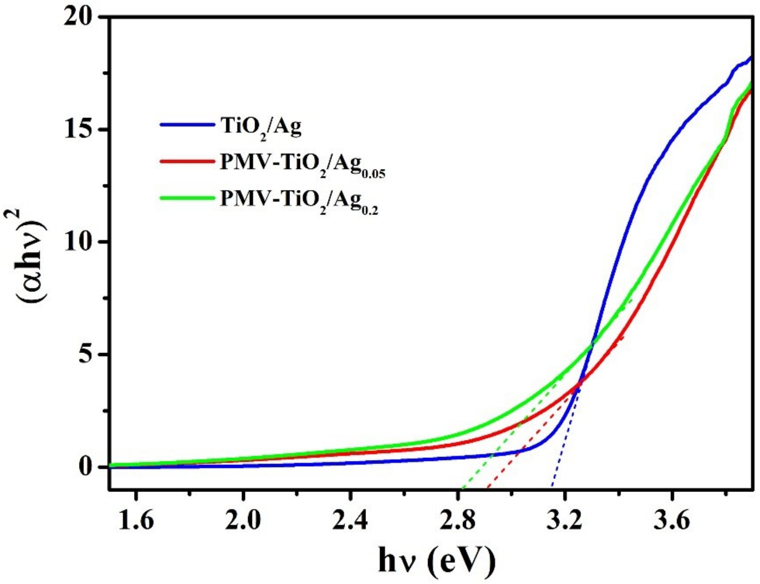
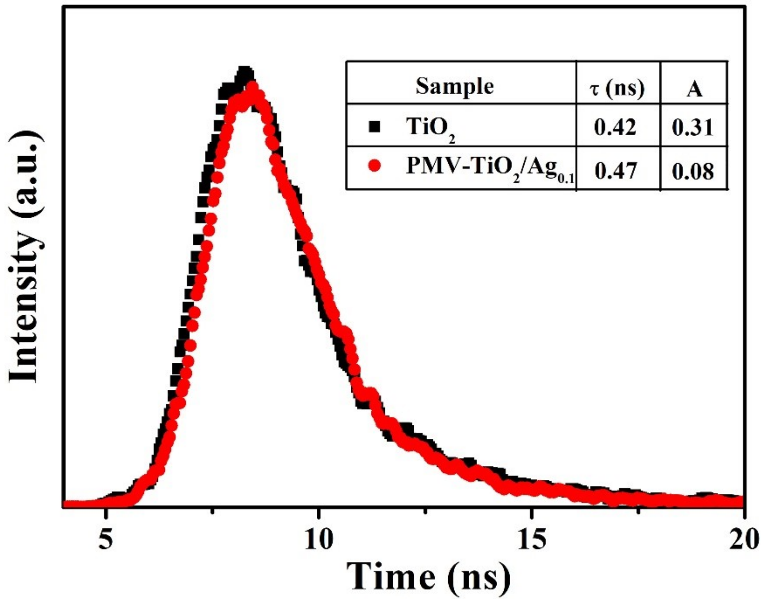


Figure S7. Calculated band gap energy by the plot of $(\alpha h\nu)^2$ *vs* $h\nu$ for different samples.



Sample	τ (ns)	A
■ TiO_2	0.42	0.31
● PMV-$TiO_2/Ag_{0.1}$	0.47	0.08

Figure S8. Time-resolved fluorescence kinetics monitored at the corresponding emission peaks of TiO_2 and PMV-$TiO_2/Ag_{0.1}$.

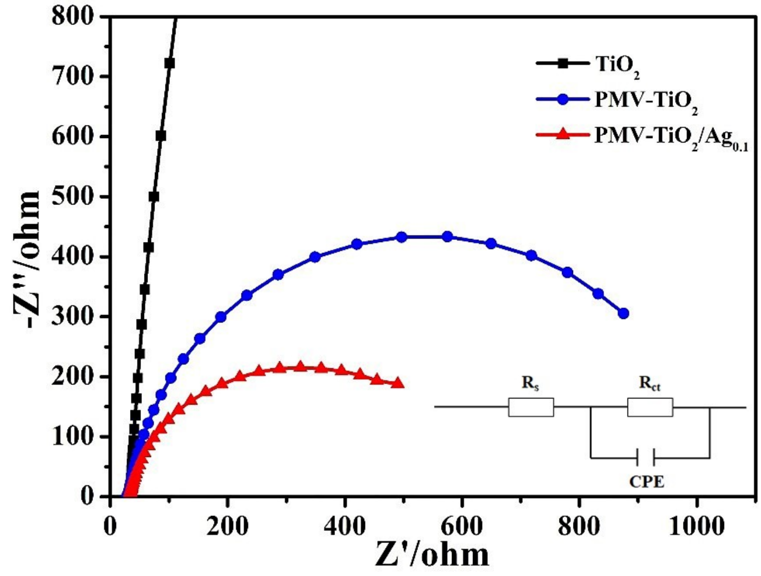


Figure S9. Electrochemical impedance spectroscopy (EIS) plots of TiO_2, PMV-TiO_2 and PMV-$TiO_2/Ag_{0.1}$.

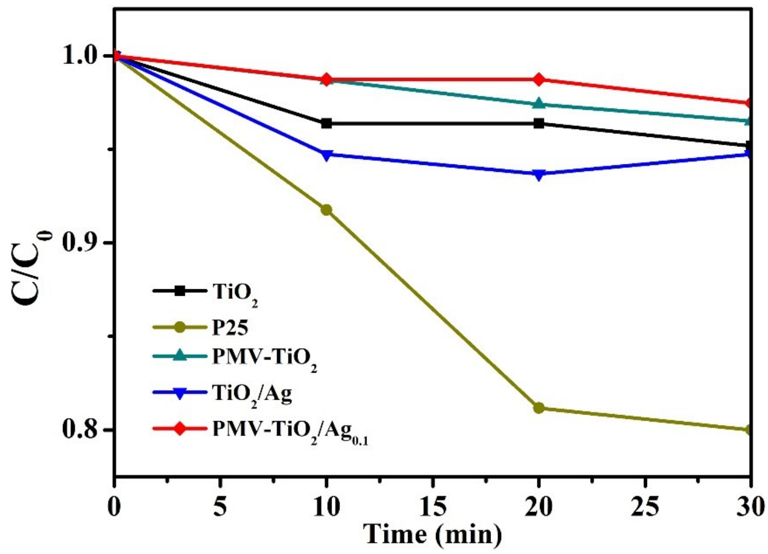


Figure S10. Adsorption curve of photocatalytic degradation of 2,4-dichlorophenol by different samples.

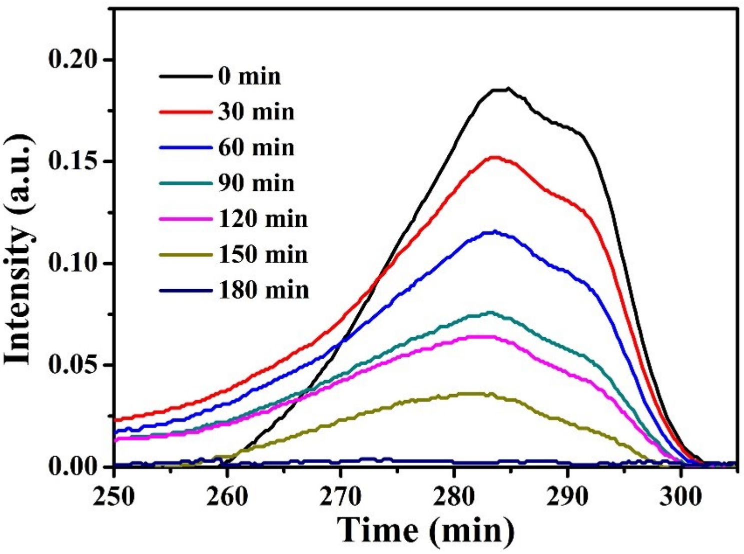


Figure S11. The curves of photocatalytic degradation of 2,4-dichlorophenol for PMV-TiO_2/$Ag_{0.1}$ under visible light irradiation (λ>420 nm).

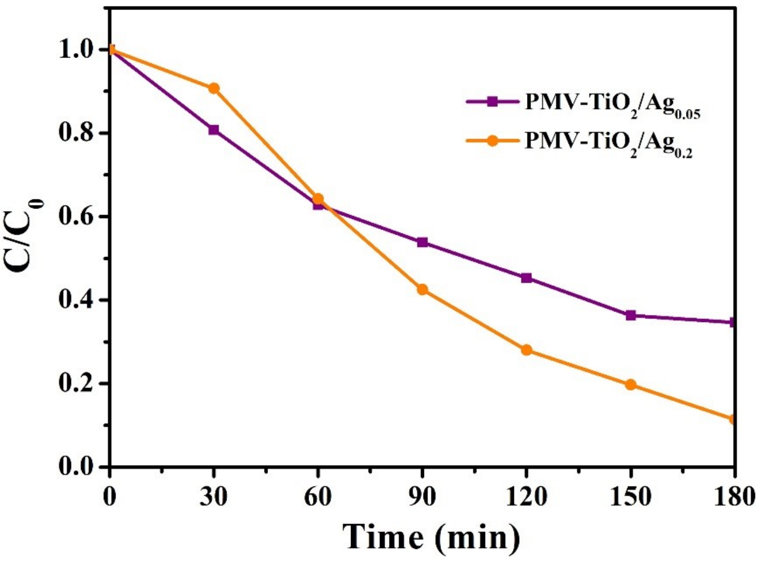


Figure S12. The photodegradation of 2,4-dichlorophenol by different samples under visible-light irradiation (λ >420nm).

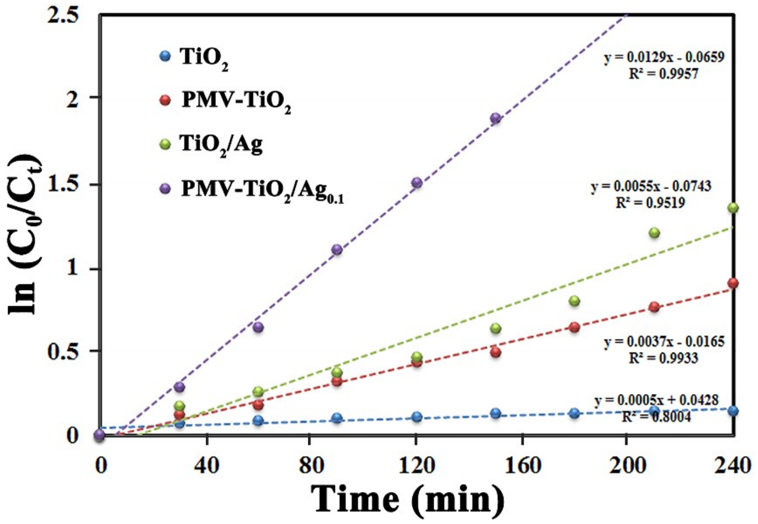


Figure S13. The plot for degradation of 2,4-DCP: $-\ln(C_t/C_0)$ as a function of time by different samples under visible-light irradiation (λ >420nm).

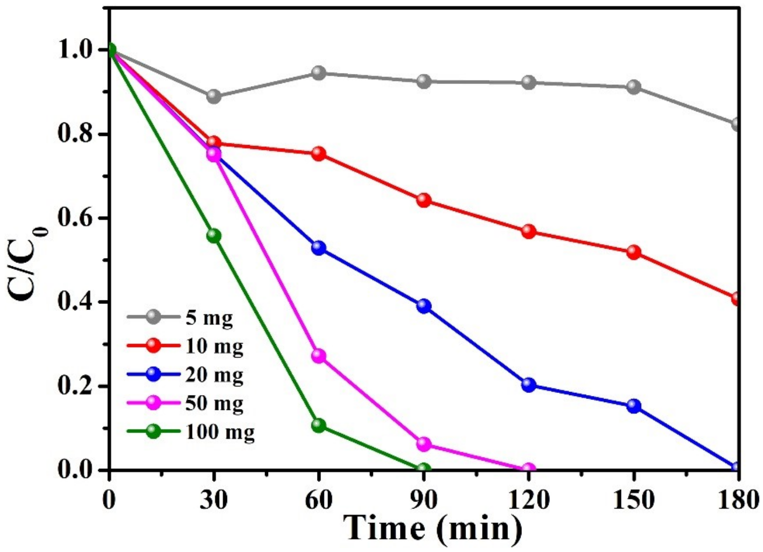


Figure S14. Optimization of catalyst dosage for photocatalytic degradation of 2,4-dichlorophenol by PMV-TiO_2/$Ag_{0.1}$.

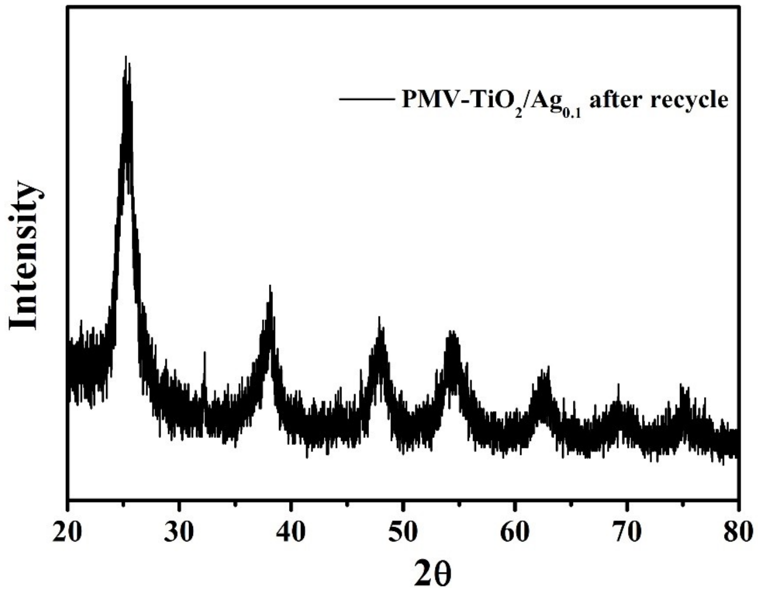


Figure S15. The XRD of PMV-TiO_2/$Ag_{0.1}$ after recycle.

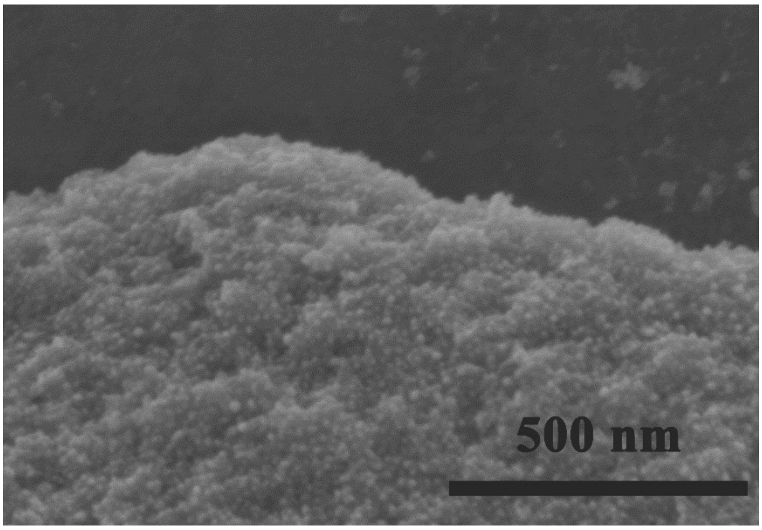


Figure S16. The SEM of PMV-$TiO_2/Ag_{0.1}$ after recycle.

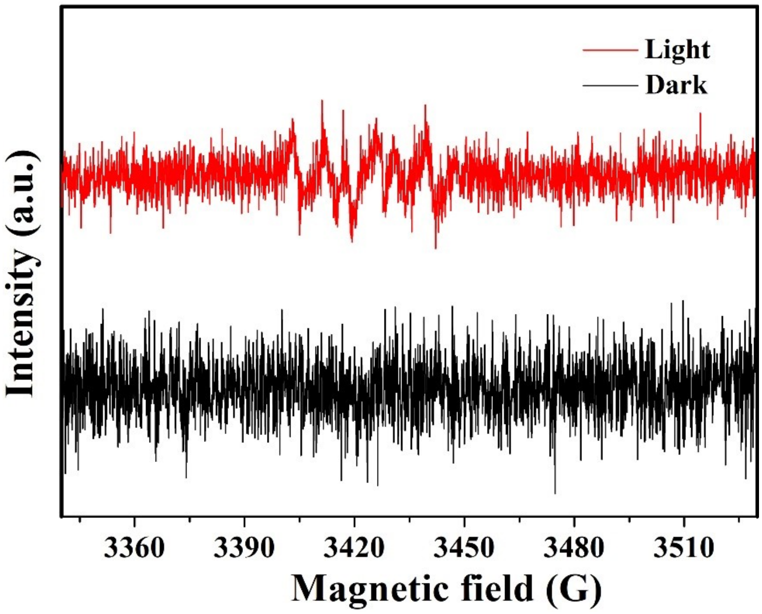


Figure S17. ESR spectra in methanol dispersion for DMPO-$\cdot O_2^-$ adduct by PMV-$TiO_2/Ag_{0.1}$.

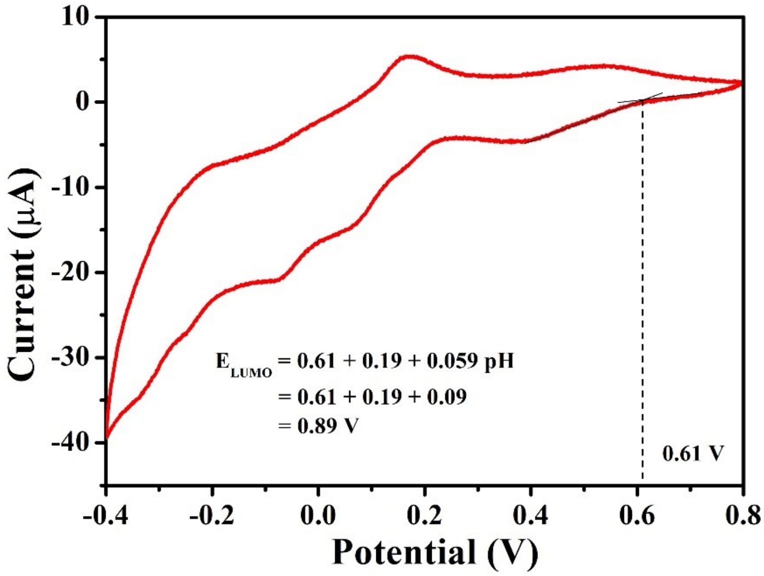


Figure S18. The cyclic voltammograms of $H_5PMo_{10}V_2O_{40}$. Cyclic voltammograms were recorded on a CHI660E Electrochemical Workstation, using glassy carbon electrode as the working electrode, a Pt wire as the counter electrode, and Ag/AgCl reference electrode. Electrolyte is 0.1M Na_2SO_4/H_2SO_4 aqueous solution (pH=1.5), the concentration of $H_5PMo_{10}V_2O_{40}$ is 1 mmol/L).

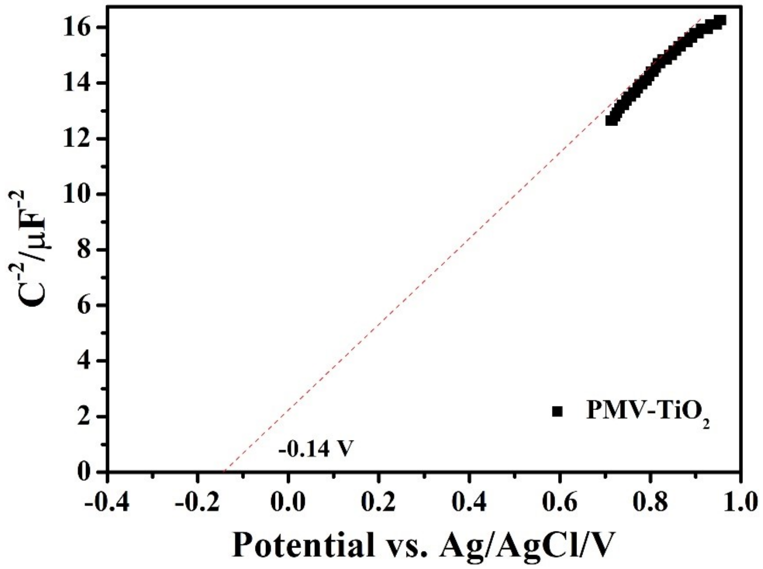


Figure S19. mott-schottky plot of PMV-TiO_2.

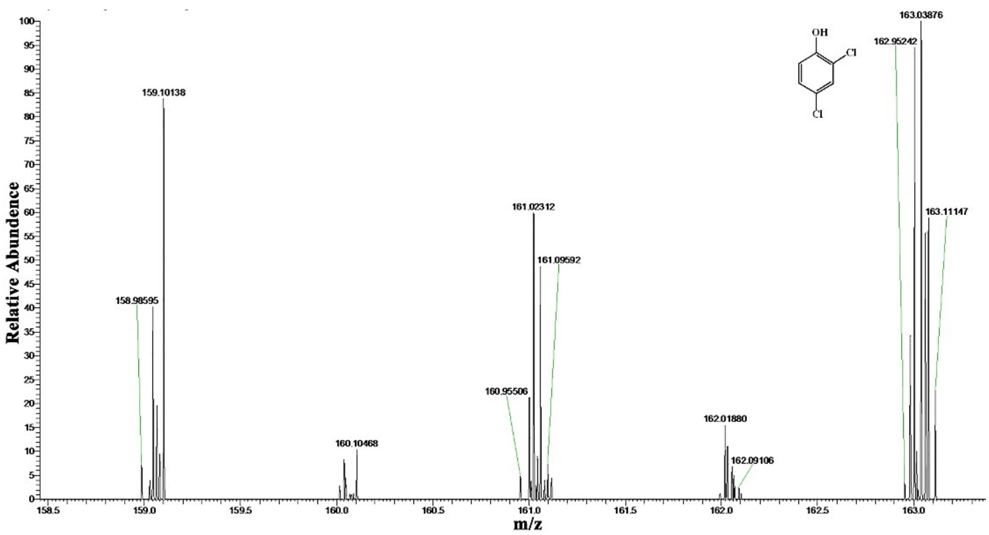


Figure S20. The main intermediate products generated during the process of photocatalytic degradation of 2,4-DCP for 0 min by PMV-TiO_2/$Ag_{0.1}$.

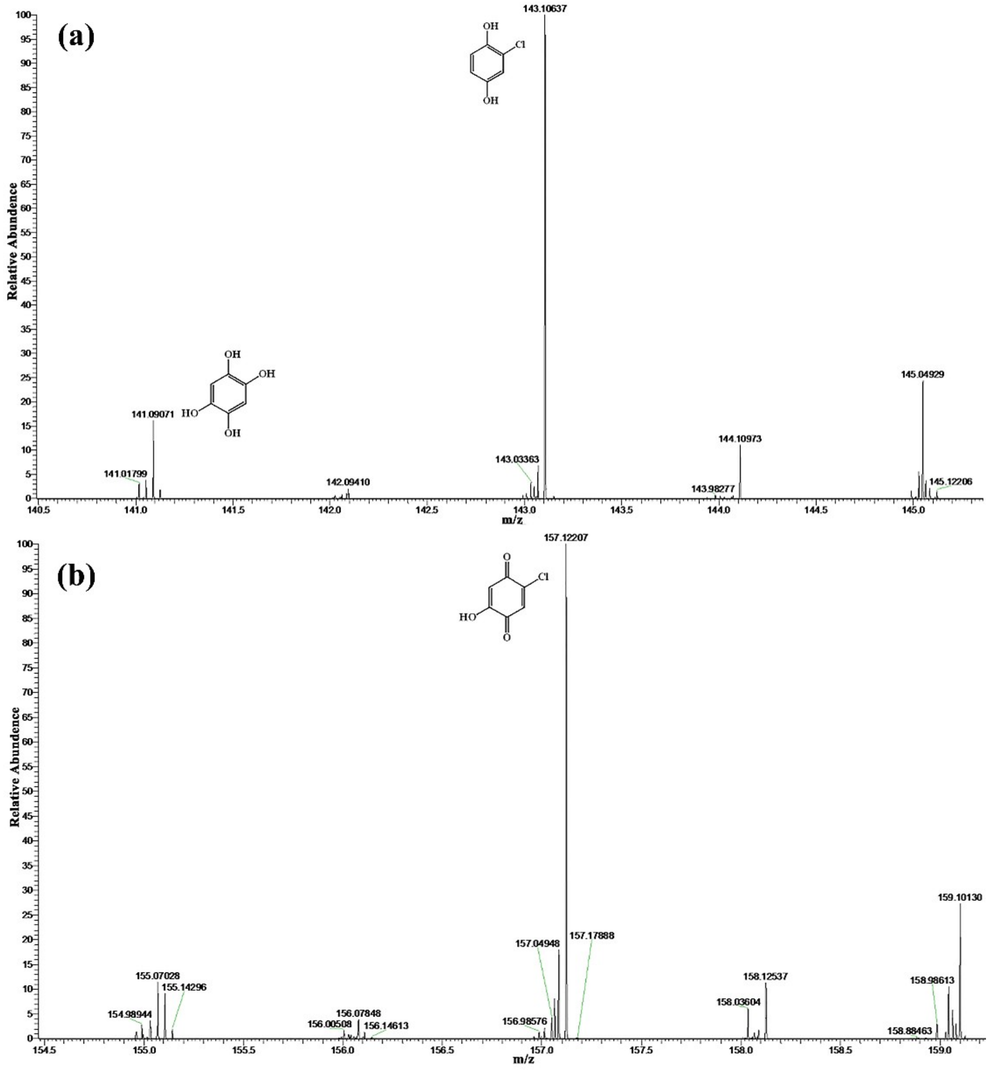


Figure S21. The main intermediate products generated during the process of photocatalytic degradation of 2,4-DCP for 80 min by PMV-TiO_2/$Ag_{0.1}$.

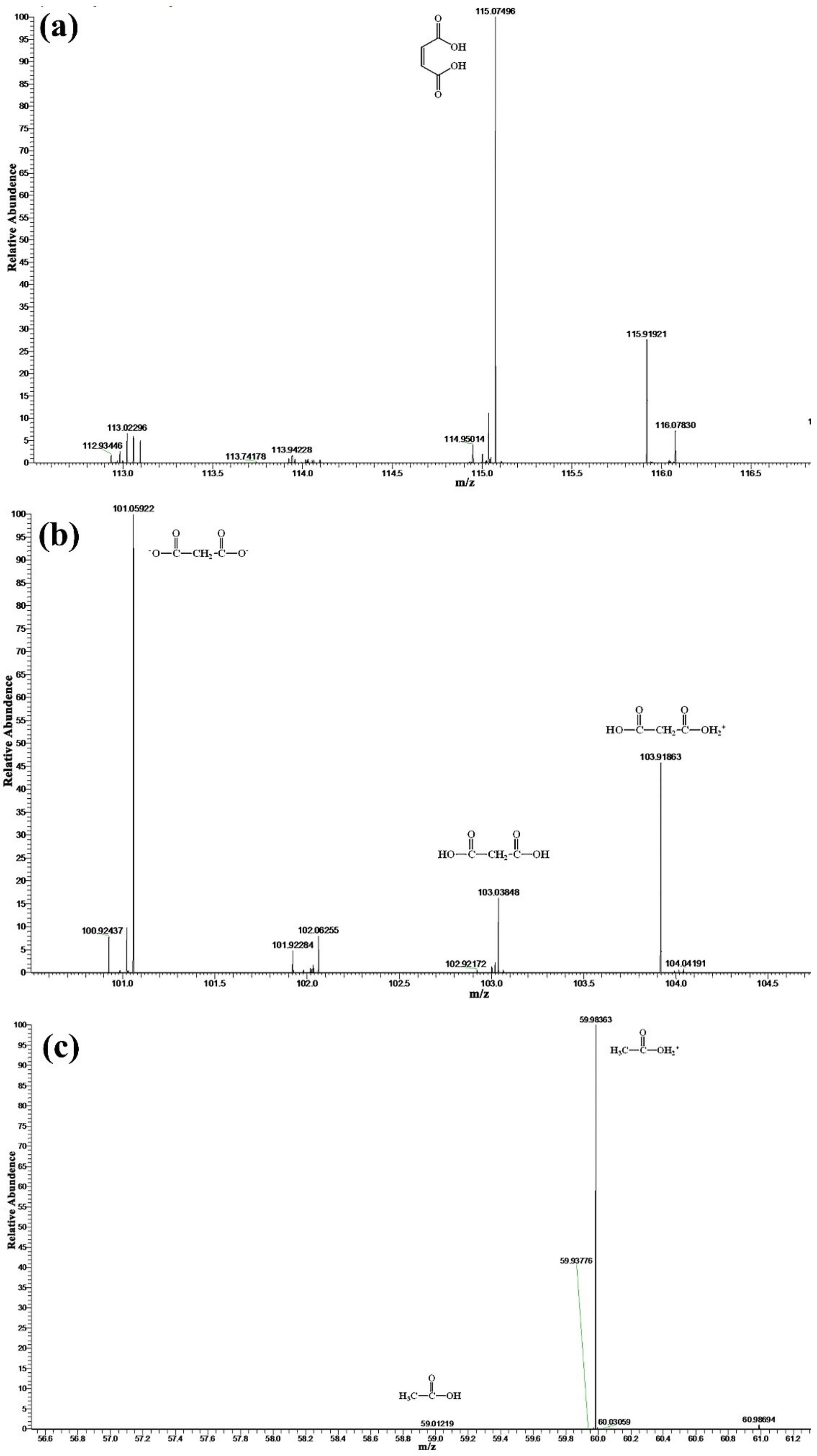


Figure S22. The main intermediate products generated during the process of photocatalytic degradation of 2,4-DCP for 180 min by PMV-TiO_2/$Ag_{0.1}$.

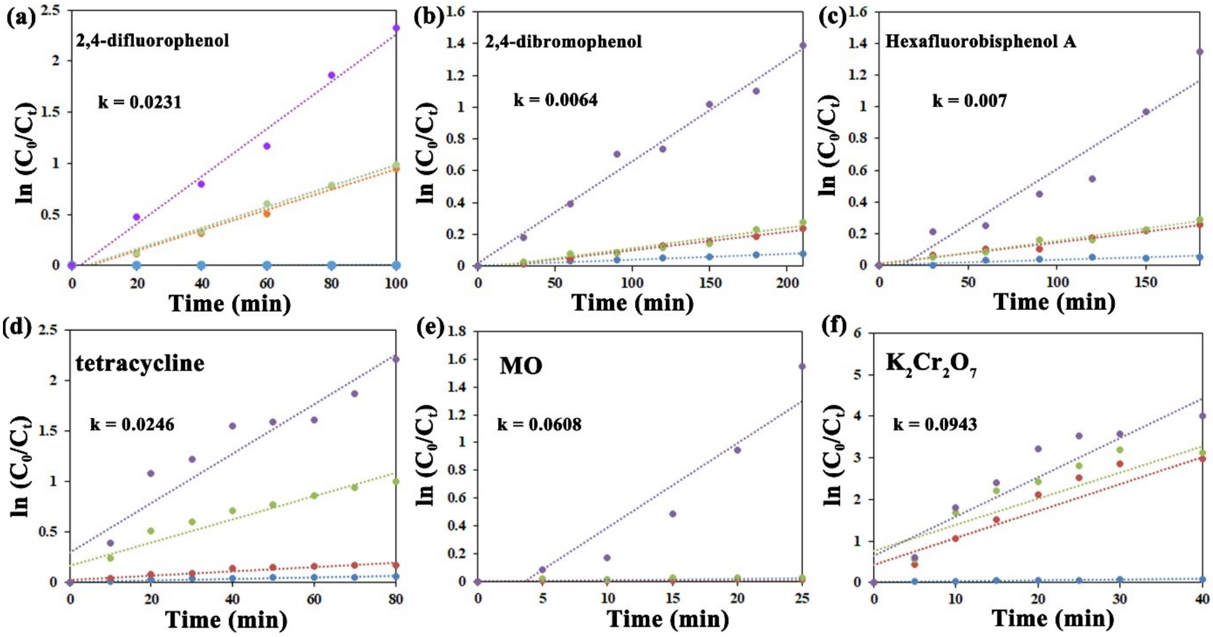


Figure S23. The plot for degradation of (a) 2,4-difluorophenol, (b) 2,4-dibromophenol, (c) hexafluorobisphenol A, (d) tetracycline, (e) MO, (f) $K_2Cr_2O_7$: $-\ln(C_t/C_0)$ as a function of time by different samples under visible-light irradiation (λ >420nm).

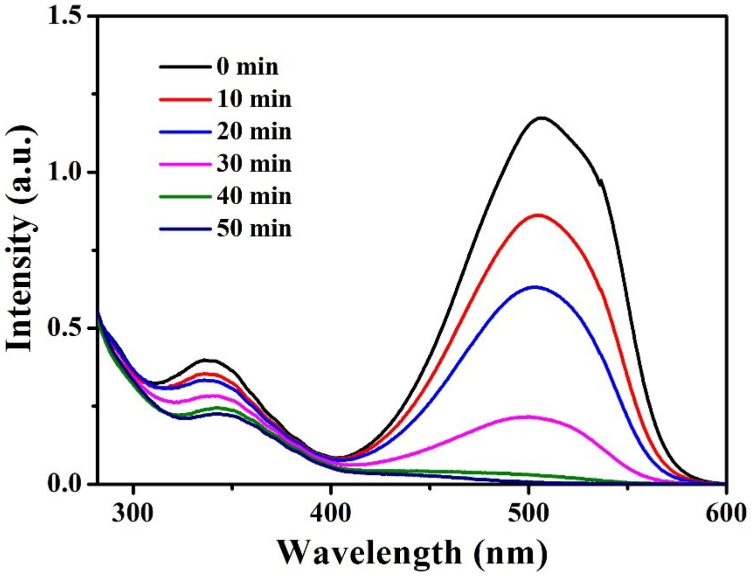
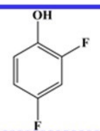
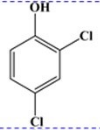
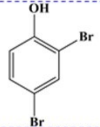
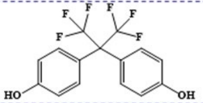
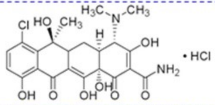
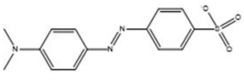


Figure S24. The plots for simultaneous degradation of Mo and reduction of $K_2Cr_2O_7$ by PMV-TiO_2/$Ag_{0.1}$.

Table S1. Photocatalytic degradation of pollutants by PMV-TiO_2/$Ag_{0.1}$.

Contaminant	concentration	Catalyst	temperature	Time	efficiency
	10 ppm	20 mg	room temperature	120 min	≈ 100 %
	10 ppm	20 mg	room temperature	180 min	≈ 100 %
	10 ppm	20 mg	room temperature	210 min	≈ 100 %
	10 ppm	50 mg	room temperature	210 min	≈ 100 %
	20 ppm	20 mg	room temperature	80 min	90 %
	20 ppm	20 mg	room temperature	30 min	≈ 100 %
$K_2Cr_2O_7$	80 ppm	20 mg	room temperature	30 min	≈ 100 %